Chapter 23
Redox Potentials and Galvanic Cells

In the last chapter, we learned a lot about Galvani potential differences across different individual interfaces and the usefulness of these potential differences, but we did not get to know how they can be measured. The problem is that it is impossible to measure the Galvani potential difference across a single interface in a half-cell directly, because an electrolyte's contact to the conductors of an electric measuring device requires a second electrode and this produces a new interface with an additional Galvani potential difference. The way out of the dilemma is the use of always the same reference half-cell, the standard hydrogen electrode, so that the measured voltage of the galvanic cell is only determined by the measuring half-cell. In this way, we obtain the so-called *redox potential* of a half-cell which represents, just like the electron potential, a measure of the strengths of reducing or oxidizing agents. The redox potentials under standard conditions are often compiled according to their values in a table, the *electrochemical series*. The combination of two arbitrary half-cells results in a galvanic cell. The reversible cell voltage of such a cell, meaning the cell voltage in equilibrium, can be described by Nernst's equation and used to predict the chemical drive, the equilibrium constant, and other thermodynamic properties of chemical reactions. Subsequently, some technically important galvanic cells will be discussed, which yield usable energy due to the spontaneous chemical reactions running inside them. In closing, the technique of potentiometry and the corresponding potentiometric titration is presented. This electroanalytical method uses the concentration dependence of the reversible cell voltage for quantitative analysis of ions.

23.1 Measuring Redox Potentials

Standard Hydrogen Electrode It is impossible to measure the Galvani potential difference across a single individual interface directly, because an electrolyte's contact to the conductors of an electric measuring device requires a second

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electrode and this produces a new interface with an additional Galvani potential difference. The usual measuring device is a voltmeter showing the sum of the two (or more) Galvani potential differences forming across the different interfaces. The total arrangement, a combination of two half-cells, is a so-called *galvanic cell*. If all the potential differences except one are kept constant, the total voltage will be influenced only by changes to this single Galvani potential difference. Measurement techniques often make use of this principle. It is possible for the Galvani potential difference to remain constant at one electrode by keeping the conditions there constant. In other words, we always use the same *reference half-cell*. In general, when reporting measured values, a *standard hydrogen electrode* (abbreviated to SHE) functions as this reference half-cell. The redox pair involved is made up of hydrogen gas at standard pressure 100 kPa, and a solution of hydrogen ions with a pH value of 0.

In Chap. 22 (Sect. 22.4), we were introduced to a simple version of such a half-cell. In the case of the reference half-cell, it is made up of a platinum sheet electrode that is immersed in an acid solution and bathed in hydrogen gas. The electrode has undergone a special platinization process that gives it a rough, strongly enlarged surface (up to 500 times). This large surface facilitates the exchange of charge between metal and solution. It should be remembered that $\mathrm{pH} = 0$ means that it is not the concentration which is prescribed, but the proton potential μ_p. Depending upon the acid used and other substance present, the $c(\mathrm{H}^+)$ value can be a little greater or smaller than 1 kmol m^{-3}, but μ_p must correspond exactly to the basic value!

Salt Bridges The different *measuring half-cells* must be conductively connected to the reference half-cell. This electric contact between the two electrolyte solutions could be accomplished with a diaphragm. In this case, however, a noticeable Galvani potential difference (up to a few 10 mV) may form across the interface between the two solutions (diffusion voltage), disturbing the measurement (compare Sect. 22.6). We use a trick in order to reduce the diffusion voltage close to a value of zero. The electrolyte solutions are not brought directly in contact but separated by a third electrolyte solution with high concentration. This third electrolyte should have only two types of ions with equal but opposite charge, and mobilities that are as similar as possible. Two examples of such electrolytes are KCl und $\mathrm{NH_4NO_3}$. The reason for this is that only a comparably small diffusion voltage will form across the interface of such a highly concentrated electrolyte and a less concentrated ion solution. If the ions are equally mobile, one type will not move faster than the other and no charging and no electric potential difference will occur. When there is a great excess of both ions, the other ions will be unable to act against these superior numbers. The diffusion voltage forming will not be exactly 0, but certainly much smaller than it would be without the intermediate electrolyte. This type of almost zero voltage connection between two electrolytes is called a *salt bridge*. The residual voltage is approximately 1 mV.

Figure 23.1 shows a practical example. The two legs of the H-shaped container are filled with saturated KCI solution. There are diaphragms at the bottom of each

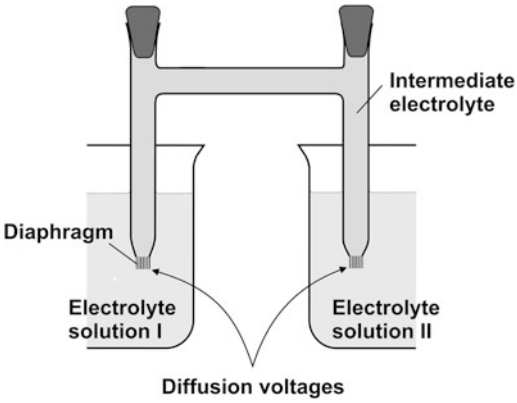


Fig. 23.1 Example of a salt bridge for producing an (almost) voltage-free connection between two electrolytes.

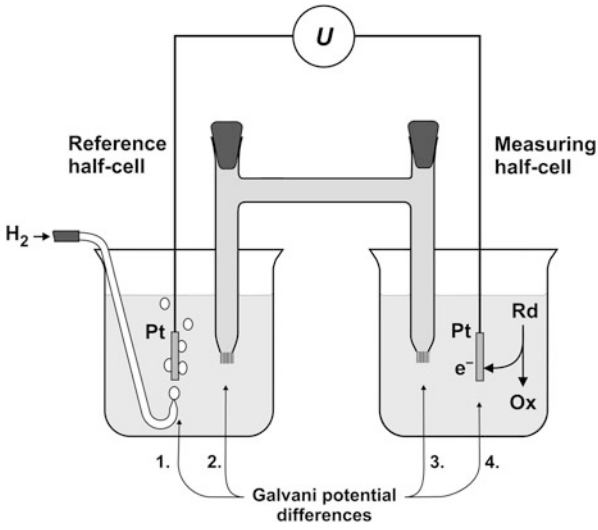


Fig. 23.2 Galvanic cell made up of a reference half-cell (standard hydrogen electrode) and a measuring half-cell containing the redox pair Rd/Ox dissolved in the corresponding electrolyte.

leg (a wad of cotton wool, a frit, a capillary, etc.). Diffusion voltages form across the diaphragms at the junctions to the different electrolyte solutions. As a rule, these voltages can be ignored, because they are small and tend to cancel each other as they have opposite signs relative to the positive direction of the current (which goes from left to right).

This arrangement of a fixed reference half-cell and salt bridge (Fig. 23.2) is frequently used in chemical measurements. It is important to perform the measurements with a current as weak as possible (ideally with no current) so that the electrochemical equilibria remain undisturbed. This can be accomplished by applying an equal counter-voltage from an external voltage source in combination with an adjustable resistor. It is much simpler and more precise, though, to use a voltmeter with high internal resistance.

Redox Potentials The total voltage U of the cell is essentially determined by the Galvani potential difference of the electrode in the measuring half-cell. U is actually the sum of four Galvani potential differences where the contributions of the two in the middle can generally be ignored. Because the first Galvani potential difference (for $T = \text{const.}$) remains constant for all the measurements, the fourth potential difference is almost the only influence upon U which is then a measure of how high the electrode is charged compared to the electrolyte. If the copper conductors of the measurement device are connected to the platinum electrode, two new Galvani potential difference will appear (so-called contact voltages between the metals), which exactly compensate for each other. The voltage between the copper conductors—shown on the measurement device—will agree with the voltage U. Therefore, U serves as the measure of the fourth Galvani potential difference which cannot be measured directly. If we keep in mind the cell notation convention from left to right when adding the four Galvani potential differences (i.e., electric potential differences), we have:

$$-U = \Delta\varphi(\text{left half-cell}) + \underbrace{\Delta\varphi(\text{left salt br.}) + \Delta\varphi(\text{right0 salt br.})}_{\approx 0} + \Delta\varphi(\text{right half-cell}).$$

If we use the abbreviations "l" and "r" for left and right, we obtain:

$$-U = \left[\varphi(\text{S})_\text{l} - \varphi(\text{Pt})_\text{l}\right] + \left[\varphi(\text{Pt})_\text{r} - \varphi(\text{S})_\text{r}\right].$$

By convention, the half-cell where the oxidation takes place has to be written on the left side and the half-cell where the reduction takes place on the right side ("**r**eduction on the **r**ight").

We form the difference $\Delta\varphi$ as we did before, meaning that the electric potential of the solution is subtracted from that of the metallic phase, and we obtain:

$$-U = -\left[\varphi(\text{Pt})_\text{l} - \varphi(\text{S})_\text{l}\right] + \left[\varphi(\text{Pt})_\text{r} - \varphi(\text{S})_\text{r}\right] = \Delta\varphi(\text{meas.}) - \Delta\varphi(\text{ref.}).$$

This measure, which has been adapted for practical purposes, is frequently used in chemistry under the name of *redox potential* E of a redox pair Rd/Ox or as *electrode potential* or *half-cell potential*. (In the following, however, we will avoid use of the term electrode potential, because it could be confused with electron potential.):

$$E = -U = \Delta\varphi(\text{meas.}) - \Delta\varphi(\text{ref.}). \tag{23.1}$$

Except for one summand, the redox potential describes the potential difference that develops between an indifferent electrode and its corresponding electrolyte in a measuring half-cell. If we use a standard hydrogen electrode as the reference electrode, we obtain

$$E = \Delta\varphi(\text{meas.}) - \Delta\overset{\circ}{\varphi}\,(\text{H}_2/\text{H}^+). \tag{23.2}$$

Due to the prevailing conditions for the hydrogen electrode, only the basic value needs to be considered. If we choose the Galvani potential difference of the standard hydrogen electrode at standard temperature $T^{\ominus} = 298\,\text{K}$ as the zero point, i.e., $\Delta\varphi^{\ominus}(\text{H}_2/\text{H}^+) = 0$, the definition $E = \Delta\varphi(\text{meas.})$ is valid. This means that the redox potential agrees with the Galvani voltage $U_{\text{Me}\to\text{S}}$ across the measuring electrode.

The redox potential measured in this way is independent of the material the indifferent electrode is made up of. If we totally replace the platinum with a different metal, possibly nickel or palladium, there will be no change to the voltage shown by the measuring device, although the Galvani voltage between electrode and electrolyte does not remain the same. The reason for this becomes clear when we replace the redox potential E by the chemical potentials of the participating substances, i.e., their electron potentials, by referring back to Eq. (22.19):

$$E = \Delta\varphi(\text{meas.}) - \Delta\varphi(\text{ref.}) = \frac{\mu_e(\text{Pt}) - \mu_e(\text{Rd/Ox})}{\mathcal{F}} - \frac{\mu_e(\text{Pt}) - \mu_e(\text{H}_2/\text{H}^+)}{\mathcal{F}}.$$

The chemical potential of the electrons in the metal drops out so that E is independent of whatever the electrode is made of:

$$E = -\frac{\mu_e(\text{Rd/Ox}) - \mu_e(\text{H}_2/\text{H}^+)}{\mathcal{F}}. \tag{23.3}$$

If we imagine the transferred electrons to be taken from the platinum, the metal ion electrodes conductively connected to the platinum of the reference electrode can be formally considered as redox electrodes. The redox potential of a copper ion electrode would then be:

$$\begin{aligned} E &= \frac{\mu_e(\text{Pt}) - \mu_e(\text{Cu/Cu}^{2+})}{\mathcal{F}} - \frac{\mu_e(\text{Pt}) - \mu_e(\text{H}_2/\text{H}^+)}{\mathcal{F}} \\ &= -\frac{\mu_e(\text{Cu/Cu}^{2+}) - \mu_e(\text{H}_2/\text{H}^+)}{\mathcal{F}}. \end{aligned}$$

The redox potential indicates up to a factor of $-\mathcal{F}$, how high the level of the electron potential $\mu_e(\text{Rd/Ox})$ is, compared to the level $\mu_e(\text{H}_2/\text{H}^+)$ of a fixed reference redox pair (where the minus sign before $-\mathcal{F}$ comes from the electrons' charge number -1). So seen, E only appears to represent an electric quantity. Actually, E describes a chemical quantity, a chemical potential difference in the same way that the difference in levels of mercury in a mercury manometer does not represent a geometric quantity but a dynamic quantity: the difference in pressure.

We were introduced to the redox pair

$$H_2|g \rightarrow 2\,H^+|w + 2e^-|Pt$$

as a general system of reference for the chemical potential of electrons under standard conditions (compare Sect. 4.4). If the temperature is allowed to vary, the chemical potentials of the substances will correspond to their basic values. In order to find the electron potential of this reference redox pair that is only dependent upon temperature, we can use the defining equation (22.18) for $\mu_e(\mathrm{Rd/Ox})$:

$$\mu_e(H_2/H^+) = \overset{\circ}{\mu}_e(H_2/H^+) = \tfrac{1}{2}\left[\overset{\circ}{\mu}(H_2;T) - 2\overset{\circ}{\mu}(H^+;T)\right]. \tag{23.4}$$

In particular, for $T^{\ominus} = 298\,\mathrm{K}$ we have $\mu_e^{\ominus}(H_2/H^+) = 0$. At standard temperature, Eq. (23.3) therefore simplifies to

$$E = -\frac{\mu_e(\mathrm{Rd/Ox})}{\mathcal{F}}. \tag{23.5}$$

Nernst's Equation In closing, we will talk about the concentration dependency of the redox potential. We obtain the following relation for a simple redox pair $\mathrm{Rd} \rightarrow \mathrm{Ox} + \nu_e e$ by inserting the $\mu_e(\mathrm{Rd/Ox})$ defining equation into Eq. (23.3):

$$E = -\frac{\dfrac{1}{\nu_e}[\mu(\mathrm{Rd}) - \mu(\mathrm{Ox})] - \overset{\circ}{\mu}_e(H_2/H^+)}{\mathcal{F}}.$$

Allowing for the mass action equation $\mu_B = \overset{\circ}{\mu}_B + RT\ln(c_B/c^{\ominus})$ for $\mu(\mathrm{Rd})$ and $\mu(\mathrm{Ox})$ yields

$$E = -\frac{\left[\overset{\circ}{\mu}(\mathrm{Rd}) - \overset{\circ}{\mu}(\mathrm{Ox})\right] - \overset{\circ}{\mu}_e\left(H_2/H^+\right)}{\nu_e \mathcal{F}} + \frac{RT}{\nu_e \mathcal{F}} \cdot \ln\frac{c(\mathrm{Ox})}{c(\mathrm{Rd})}. \tag{23.6}$$

By abbreviating the first term (the *basic value* of the redox potential) to $\overset{\circ}{E}$, we obtain the corresponding Nernst equation:

$$E = \overset{\circ}{E} + \frac{RT}{\nu_e \mathcal{F}} \cdot \ln\frac{c(\mathrm{Ox})}{c(\mathrm{Rd})}. \tag{23.7}$$

As we would expect from relation (23.2), the redox potential shows the same concentration dependency as the Galvani potential difference [Eq. (22.23)]. The various versions of Nernst's equation generally exhibit great similarity to the proton level equation [Eq. (7.12)]. This equation describes the dependency of proton potential μ_p upon the ratio of acid and base concentrations, i.e., upon $c(\mathrm{Ad})/c(\mathrm{Bs})$. The similarity results from the direct relation of the Galvani potential difference of a half-cell or its redox potential with the electron potential μ_e [Eqs. (22.19) or (23.3)], which is formally closely related to the proton potential.

The frequently used "*decadic*" version of Eq. (23.7) can be obtained by going from the natural logarithm to the logarithm to base 10 in the second term (the so-called *mass action term* of the redox potential):

$$E = \overset{\circ}{E} + \frac{E_N(T)}{\nu_e} \cdot \lg \frac{c(\mathrm{Ox})}{c(\mathrm{Rd})}. \tag{23.8}$$

The following is valid for the factor

$$E_N(T) := \frac{RT \ln 10}{\mathcal{F}} \tag{23.9}$$

at the standard temperature $T^{\ominus} = 298\,\mathrm{K}$:

$$E_N^{\ominus} = E_N(T^{\ominus}) = \frac{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K} \times 2.303}{96,485\,\mathrm{C\,mol^{-1}}} = 0.059\,\mathrm{V}.$$

In the case of the composite redox pair $\mathrm{Rd} \rightarrow \mathrm{Ox} + \nu_e \mathrm{e}$, where Rd stands for the combination of substances $\mathrm{Rd}' + \mathrm{Rd}'' + \ldots$ and Ox stands for the combination $\mathrm{Ox}' + \mathrm{Ox}'' + \ldots$, we must correspondingly alter the Nernst equation [compare derivation of Eq. (22.24)]:

$$E = \overset{\circ}{E}(\mathrm{Rd/Ox}) + \frac{E_N(T)}{\nu_e} \cdot \lg \frac{c_r(\mathrm{Ox}')^{\nu_{\mathrm{Ox}'}} \cdot c_r(\mathrm{Ox}'')^{\nu_{\mathrm{Ox}''}} \cdot \ldots}{c_r(\mathrm{Rd}')^{\nu_{\mathrm{Rd}'}} \cdot c_r(\mathrm{Rd}'')^{\nu_{\mathrm{Rd}''}} \cdot \ldots}.$$

or abbreviated

$$E = \overset{\circ}{E}(\mathrm{Rd/Ox}) + \frac{E_N(T)}{\nu_e} \cdot \lg \frac{\prod_{i=1}^{k} c_r(\mathrm{Ox}_i)^{\nu_{\mathrm{Ox}_i}}}{\prod_{j=1}^{l} c_r(\mathrm{Rd}_j)^{\nu_{\mathrm{Rd}_j}}}.$$

Using the redox potential of the pair made up of bivalent and trivalent iron as a simple example we obtain with $\nu_e = 1$:

$$E = \overset{\circ}{E}(\mathrm{Fe^{2+}/Fe^{3+}}) + E_N \cdot \lg \frac{c(\mathrm{Fe^{3+}})}{c(\mathrm{Fe^{2+}})}$$

or, at the standard temperature $T^{\ominus} = 298\,\mathrm{K}$,

$$E = E^{\ominus}(\mathrm{Fe^{2+}/Fe^{3+}}) + 0.059\,\mathrm{V} \cdot \lg \frac{c(\mathrm{Fe^{3+}})}{c(\mathrm{Fe^{2+}})}.$$

Increasing $c(\mathrm{Fe^{3+}})/c(\mathrm{Fe^{2+}})$ tenfold leads to a 59 mV increase of E. The concentration dependency of the redox potential $E(\mathrm{Fe^{2+}/Fe^{3+}})$ is shown in Fig. 23.3.

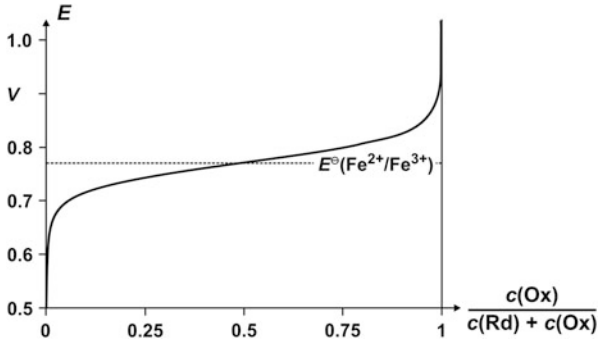


Fig. 23.3 Concentration dependency of the redox potential E for the pair Fe^{2+}/Fe^{3+} at 298 K. [The abscissa shows the fraction in oxidized form, meaning the ratio $c(\mathrm{Ox})/(c(\mathrm{Rd})+c(\mathrm{Ox}))$].

If the concentrations of the oxidized and reduced forms of the redox pair are equal $\left[c(\mathrm{Ox}) = c(\mathrm{Rd}) \text{ or } c(\mathrm{Ox})/(c(\mathrm{Rd}) + c(\mathrm{Ox})) = 0.5\right]$, then according to Eq. (23.7), the redox potential will correspond to the standard value $E^{\ominus}$ (because $\ln 1 = 0$). However, if the concentration of the oxidizing agent is greater than that of the corresponding reducing agent, the redox potential will be shifted to higher values, and if it is smaller, there will be a shift to lower values. This is expected because when we have a high concentration $c(\mathrm{Ox})$, there will be a strong tendency to "snatch" electrons from the measuring electrode, thereby giving it a positive potential. On the other hand, if $c(\mathrm{Rd})$ is high, the tendency will be to emit electrons to the measuring electrode, resulting in a lowering of its potential [$\ln(c(\mathrm{Ox})/c(\mathrm{Rd}))$ will be negative for $c(\mathrm{Ox}) < c(\mathrm{Rd})$].

In contrast, the redox potential of the hydrogen electrode results in

$$E = \overset{\circ}{E}(\mathrm{H_2}/\mathrm{H^+}) + \frac{E_\mathrm{N}}{2} \cdot \lg \frac{(c_{\mathrm{H^+}}/c^{\ominus})^2}{p_{\mathrm{H_2}}/p^{\ominus}}$$

with $\nu_\mathrm{e} = 2$. Because of $E^{\ominus}(\mathrm{H_2}/\,\mathrm{H^+}) = 0$, the equation simplifies to

$$E = \frac{0.059\,\mathrm{V}}{2} \cdot \lg \frac{(c_{\mathrm{H^+}}/c^{\ominus})^2}{p_{\mathrm{H_2}}/p^{\ominus}}.$$

Electrochemical Series Some redox potentials under standard conditions ($T^{\ominus} = 298\,\mathrm{K}$, $p^{\ominus} = 100\,\mathrm{kPa}$, $c^{\ominus} = 1\ \mathrm{kmol\,m^{-3}}$ in aqueous solutions) have been compiled in the following table (Table 23.1). This kind of sequence of standard redox potentials is also called the *electrochemical series*. The half-cells in question have been characterized by the corresponding "Stockholm convention" of 1953. In this convention, a phase boundary is denoted by a single vertical line.

Equation (23.6) tells us that although the standard value of a redox potential $E^{\ominus}$ depends upon the type of reference electrode being used, it is otherwise a characteristic quantity for the redox pair because of its direct dependency upon the electron potential. Just like the electron potential, it represents a measure of

Table 23.1 Redox potentials at standard conditions (298 K, 100 kPa, 1 kmol m^{-3} in an aqueous solution), based upon a standard hydrogen electrode (from: Lide D R (ed) (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton).

Half cell	Electrode reaction	$E^{\ominus}$(V)
$Li\|Li^+$	$Li^+ + e^- \rightleftarrows Li$	−3.0401
$Cs\|Cs^+$	$Cs^+ + e^- \rightleftarrows Cs$	−3.026
$Rb\|Rb^+$	$Rb^+ + e^- \rightleftarrows Rb$	−2.98
$K\|K^+$	$K^+ + e^- \rightleftarrows K$	−2.931
$Ca\|Ca^{2+}$	$Ca^{2+} + 2\,e^- \rightleftarrows Ca$	−2.868
$Na\|Na^+$	$Na^+ + e^- \rightleftarrows Na$	−2.71
$Mg\|Mg^{2+}$	$Mg^{2+} + 2\,e^- \rightleftarrows Mg$	−2.372
$Al\|Al^{3+}$	$Al^{3+} + 3\,e^- \rightleftarrows Al$	−1.662
$Zn\|Zn^{2+}$	$Zn^{2+} + 2\,e^- \rightleftarrows Zn$	−0.7618
$Fe\|Fe^{2+}$	$Fe^{2+} + 2\,e^- \rightleftarrows Fe$	−0.447
$Cd\|Cd^{2+}$	$Cd^{2+} + 2\,e^- \rightleftarrows Cd$	−0.4030
$Ni\|Ni^{2+}$	$Ni^{2+} + 2\,e^- \rightleftarrows Ni$	−0.257
$Pb\|Pb^{2+}$	$Pb^{2+} + 2\,e^- \rightleftarrows Pb$	−0.1262
$Cu\|Cu^{2+}$	$Cu^{2+} + 2\,e^- \rightleftarrows Cu$	+0.3419
$Ag\|Ag^+$	$Ag^+ + e^- \rightleftarrows Ag$	+0.7996
$2\,Hg\|Hg_2^{2+}$	$Hg_2^{2+} + 2\,e^- \rightleftarrows 2\,Hg$	+0.7973
$Au\|Au^+$	$Au^+ + e^- \rightleftarrows Au$	+1.692
$Pt\|H_2\|OH^-$	$2\,H_2O + 2\,e^- \rightleftarrows H_2 + 2\,OH^-$	−0.8277
$Pt\|Cr^{2+}, Cr^{3+}$	$Cr^{3+} + e^- \rightleftarrows Cr^{2+}$	−0.407
$Pt\|H_2\|H^+$	$2H^+ + 2\,e^- \rightleftarrows H_2$	0.00000
$Pt\|Sn^{2+}, Sn^{4+}$	$Sn^{4+} + 2\,e^- \rightleftarrows Sn^{2+}$	+0.151
$Pt\|Cu^+, Cu^{2+}$	$Cu^{2+} + e^- \rightleftarrows Cu^+$	+0.153
$Pt\|[Fe(CN)_6]^{4-}, [Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{3-} + e^- \rightleftarrows [Fe(CN)_6]^{4-}$	+0.358
$Pt\|O_2\|OH^-$	$O_2 + H_2O + 2\,e^- \rightleftarrows H_2 + 2OH^-$	+0.401
$Pt\|I_2\|I^-$	$I_2 + 2\,e^- \rightleftarrows 2I^-$	+0.5355
$Pt\|Fe^{2+}, Fe^{3+}$	$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.771
$Pt\|O_2\|H^+$	$½O_2 + 2H^+ + 2\,e^- \rightleftarrows H_2O$	+1.229
$Pt\|Cl_2\|Cl^-$	$Cl_2 + 2\,e^- \rightleftarrows 2Cl^-$	+1.35827
$Pt\|F_2\|F^-$	$F_2 + 2\,e^- \rightleftarrows 2F^-$	+2.866
$Pb\|PbSO_4\|SO_4^{2-}$	$PbSO_4 + 2\,e^- \rightleftarrows Pb + SO_4^{2-}$	−0.3588
$Ag\|AgI\|I^-$	$AgI + e^- \rightleftarrows Ag + I^-$	−0.15224
$Ag\|AgCl\|Cl^-$	$AgCl + e^- \rightleftarrows Ag + Cl^-$	+0.22233
$Hg\|Hg_2Cl_2\|Cl^-$	$Hg_2Cl_2 + 2\,e^- \rightleftarrows 2\,Hg + 2Cl^-$	+0.26808

the strengths of the reducing or the oxidizing agents. A strongly negative value of the redox potential means that the corresponding redox pair is highly reductive and will have a strong tendency to "press" electrons onto the measuring electrode, producing a high "electron pressure." Correspondingly, a more strongly reductive redox pair with a lower redox potential can force electrons onto a "weaker" pair in contact with it. A look at the redox potentials tells us that the redox pair Sn^{2+}/Sn^{4+} is more strongly reductive than the redox pair Fe^{2+}/Fe^{3+} $\left[E^{\ominus}(Sn^{2+}/Sn^{4+}) = +0.151\,V;\ E^{\ominus}(Fe^{2+}/Fe^{3+}) = +0.771\,V\right]$ (compare Sect. 22.4).

Reference Electrodes The advantage of the standard hydrogen electrode used as the reference for a given redox potential is that its equilibrium Galvani potential difference adjusts quickly and reproducibly. It is, however, rather complicated to deal with because, among other things, a bottle containing oxygen-free (and highly explosive) hydrogen gas is necessary.

A film electrode made up of silver–silver chloride also has a well-reproducible Galvani potential difference, as we saw in Sect. 22.5. Because it is much easier to handle than a standard hydrogen electrode, it is the preferred reference electrode. Its structure is rather simple: Silver chloride is precipitated directly onto a silver wire as a thin layer by electrolysis—the wire is immersed in a highly concentrated chloride solution—mostly potassium chloride (saturated or 3 kmol m^{-3}). The concentration of Cl^- ions determines the Galvani potential difference. In practice and for simplicity (Fig. 23.4), the electrolyte solutions in the reference half-cell and the (integrated) salt bridge are made equal. The diaphragm between these two parts can therefore be left out and only one diaphragm at the measuring cell is necessary. The potassium and chloride ions are about equally mobile and highly concentrated, so no noticeable diffusion voltage builds up at this point of contact.

Because of the constant potential differences at the charge exchanging interfaces, the *silver–silver chloride reference electrode* forms a kind of "pluggable connector" between the metallic conductors and the outer solution. This makes it possible to easily determine the variable potential differences in the circuit. This

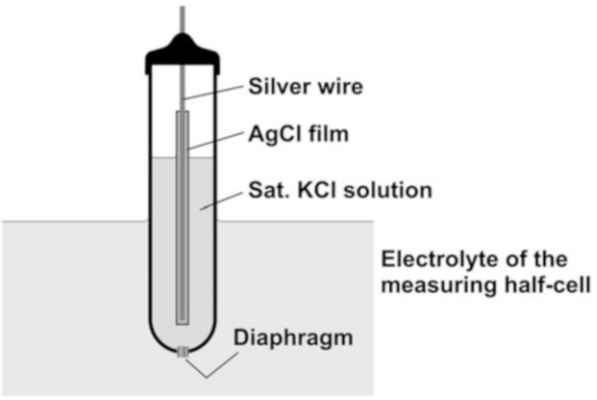


Fig. 23.4 Practical construction of a silver–silver chloride reference electrode.

allows us to determine the Galvani potential difference of a measuring half-cell relative to this new reference point and then convert to the standard hydrogen electrode (SHE). However, the potential differences of the silver–silver chloride electrode relative to the SHE must be known. At 298 K and using saturated KCI solution as the electrolyte, it is +0.1976 V.

In principle, a *calomel electrode* is very similar. Here, mercury (Hg) and low soluble mercury(I)chloride (calomel, Hg_2Cl_2) replace Ag and AgCl. The liquidity of mercury necessitates a somewhat different arrangement, but the process is the same.

23.2 Cell Voltage

Until now, we have been dealing mostly with reactions of the type $\mathrm{Rd} \rightarrow \mathrm{Ox} + \nu_e e$. Since free electrons cannot be obtained under the usual laboratory conditions, these kinds of processes never happen alone, but always occur in pairs—as we have mentioned already. Therefore, a complete *redox reaction* is composed of two *half-reactions*,

$$\mathrm{Rd} \rightarrow \mathrm{Ox} + \nu_e e \qquad \text{and} \qquad \mathrm{Rd}^* \rightarrow \mathrm{Ox}^* + \nu_e e,$$

where the first runs backward and the second runs forward or vice versa. In order for coupling to be possible, the two half-reactions must be formulated so that the conversion number ν_e of the electrons is the same in both of them. If necessary, this can be accomplished by multiplying the conversion formulas by the appropriate numerical factors. The resulting total reaction would then be:

$$\mathrm{Rd} + \mathrm{Ox}^* \rightarrow \mathrm{Ox} + \mathrm{Rd}^*.$$

The half-reactions of the reaction $2\,Fe^{3+}|w + Sn^{2+}|w \rightarrow 2\,Fe^{2+}|w + Sn^{4+}|w$ (compare Experiment 22.1) must be correspondingly formulated as follows:

$$Sn^{2+}|w \rightarrow Sn^{4+}|w + 2\,e^- \qquad \text{and} \qquad 2\,Fe^{2+}|w \leftarrow 2\,Fe^{3+}|w + 2\,e^-.$$

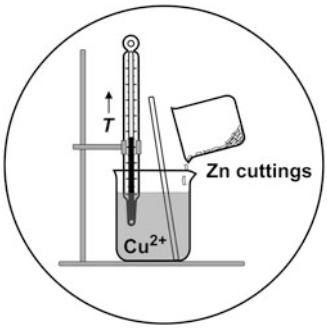
This example shows how a reaction can run under conditions where the electrons are directly exchanged between the substances. A further example is the reaction of zinc cuttings with a copper sulfate solution (Experiment 23.1),

$$Zn|s + Cu^{2+}|w \rightarrow Zn^{2+}|w + Cu|s,$$

where the following half-reactions,

$$Zn|s \rightarrow Zn^{2+}|w + 2\,e^- \qquad \text{and} \qquad Cu|s \leftarrow Cu^{2+}|w + 2\,e^-,$$

Experiment 23.1 *Reduction of Cu^{2+} ions by zinc*: When zinc cuttings are poured into a solution containing copper ions, they precipitate densely and immediately turn black. The precipitate then slowly turns coppery brown while the solution's color successively changes from blue to green to brown and, finally, colorless. Simultaneously, the temperature rises considerably.



must be considered [respective redox potentials: $E^{\ominus}(\mathrm{Zn}/\mathrm{Zn}^{2+}) = -0.7618\,\mathrm{V}$, $E^{\ominus}(\mathrm{Cu}/\mathrm{Cu}^{2+}) = +0.3419\,\mathrm{V}$].

According to Eq. (8.18), the energy W_ξ necessary for a small conversion $\Delta\xi$ of the total reaction is

$$W_\xi = -\mathcal{A} \cdot \Delta\xi = \left[\mu(\mathrm{Cu}) + \mu(\mathrm{Zn}^{2+}) - \mu(\mathrm{Zn}) - \mu(\mathrm{Cu}^{2+})\right] \cdot \Delta\xi, \qquad (23.10)$$

in which energy $W_\xi < 0$ is released during the spontaneous process ($\mathcal{A} > 0$). This released energy is dissipated and entropy is generated, which is expressed by a warming of the reaction mixture.

The two half-reactions can also be spatially separated from each other by dividing them into the two half-cells of a galvanic cell where they are connected to each other by an exterior circuit. For example, the so-called *Daniell cell* (Fig. 23.5) is composed of a Zn and a Cu electrode that are immersed in corresponding Zn^{2+} or Cu^{2+} solutions whereby these electrolyte solutions are in contact with each other through a diaphragm. To avoid diffusion voltages, a salt bridge can be used instead.

The gradient of the chemical potential continues to drive the reaction

$$\mathrm{Zn|s} + \mathrm{Cu}^{2+}\mathrm{|w} \rightarrow \mathrm{Zn}^{2+}\mathrm{|w} + \mathrm{Cu|s}.$$

However, the reactants can no longer reach each other so easily because they are separated by a "wall" (the electrolyte solutions) that ions can permeate but electrons cannot. The only possibility is for the ions and electrons to go "separate ways." While the ions can migrate into the electrolyte solution, the electrons must be diverted through the external circuit. Zinc ions at the zinc electrode go into the solution, meaning that oxidation takes place, so we know we are dealing with an anode (Fig. 23.6). The accumulation of electrons caused by the electrons left behind gives this electrode a negative charge. At the copper electrode, on the other hand,

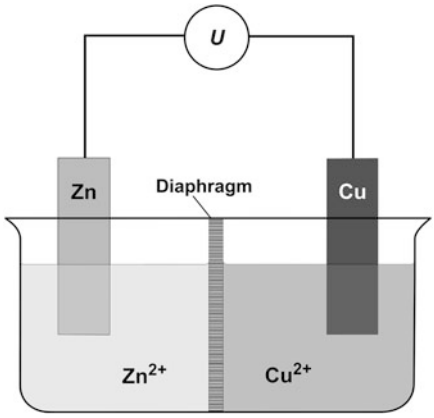


Fig. 23.5 Schematic of a Daniell cell.

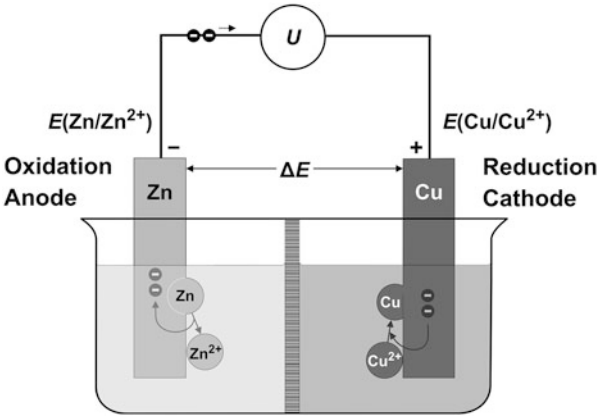


Fig. 23.6 Electrode processes in a Daniell cell and nomenclature.

copper ions are deposited in the form of neutral copper. This means that the ions are reduced (cathode). The "electron suction" caused by the consumption of electrons gives this electrode a positive charge and an electric voltage then develops between the two electrodes. However, immediately after even extremely small amounts of ions have transferred, electrochemical equilibrium occurs at the electrodes (compare Sect. 22.3).

Using the example of a Daniell cell, we will consider the conventions used in representing galvanic cells. In a cell diagram, as previously mentioned, a vertical line symbolizes a phase boundary. A dashed line represents a diaphragm through which both electrolyte solutions in the half-cell are in contact with each other. If the diffusion voltage is minimized, possibly by the use of a salt bridge, a dashed double

line will stand for this. Therefore, depending upon the setup, the abbreviation for a Daniell cell is

$$\mathrm{Zn|Zn^{2+}\,\vdots\,Cu^{2+}|Cu} \quad \text{or} \quad \mathrm{Zn|Zn^{2+}\,\vdots\,\vdots\,Cu^{2+}|Cu}.$$

If the direction of a reaction is arbitrarily chosen when writing the conversion formula of a cell reaction, for example,

$$\mathrm{Zn|s + Cu^{2+}|w \rightarrow Zn^{2+}|w + Cu|s},$$

without first predicting how it may spontaneously run, the redox pair will be oxidized in the first partial reaction, and in the other partial reaction, the other pair will be reduced:

$$\begin{aligned} &\text{Oxidation(anode):} \quad \mathrm{Zn|s \rightarrow Zn^{2+}|w + 2\,e^-} \quad (\text{left, in the cell diagram}),\\ &\text{Reduction(cathode):} \quad \mathrm{Cu^{2+}|w + 2\,e^- \rightarrow Cu|s} \quad (\text{right, in the cell diagram}). \end{aligned}$$

If the reaction actually does run spontaneously in the chosen direction, positive charge will be transported through the cell from left to right (and because of this, from right to left through the external part of the electric circuit). The electrode on the right is the positive terminal. When we measure the voltage of this cell for zero current flowing in order not to disturb the equilibrium, it corresponds to the difference of the cathode and anode potentials:

$$-U = \Delta E = E(\text{cathode}) - E(\text{anode}) = E(\mathrm{Cu/Cu^{2+}}) - E(\mathrm{Zn/Zn^{2+}}). \quad (23.11)$$

As mentioned in the previous section, zero current flowing can be realized by using of a voltmeter with high internal resistance or by applying an equal counter-voltage from an external voltage source in combination with an adjustable resistor. Even if the second method, the classical Poggendorff compensation method, is more complicated it is interesting from a theoretical point of view because it illustrates the thermodynamic relevance of ΔE. A very slight, in principle infinitesimally small, decrease of the opposing voltage will allow the reaction to proceed in the spontaneous direction; an infinitesimal increase of the opposing voltage, however, will force the reaction backward. Only if the opposing voltage exactly corresponds to the potential difference generated by the cell, the cell properties are determined under reversible conditions and, therefore, in electrochemical equilibrium.

ΔE is often called the *electromotive force* (*EMF*). But we will avoid using this term because it is potentially misleading: An electric potential difference is not a force! Instead, we will use the term "reversible cell voltage" ("zero-current cell voltage", "open circuit voltage"). We will consider ΔE to be positive in the case discussed here. At standard conditions, the resulting value for the Daniell cell is

$$\Delta E^{\ominus} = E^{\ominus}(\mathrm{Cu/Cu^{2+}}) - E^{\ominus}(\mathrm{Zn/Zn^{2+}}) = +0.3402\,\mathrm{V} - (-0.7628\,\mathrm{V}) \\ = +1.103\,\mathrm{V}.$$

However, if the reaction does not run spontaneously in the chosen direction, as would happen in the case of

$$\mathrm{Zn^{2+}|w + Cu|s \rightarrow Zn|s + Cu^{2+}|w},$$

the cell voltage defined by convention changes its sign and ΔE becomes negative.

In summary: In a spontaneous reaction, the electrode with the higher redox potential is the cathode and the one with lower redox potential is the anode. In other words, the redox pair with the higher redox potential will be reduced. The redox pair with the lower redox potential, however, will be oxidized.

We know (compare Sect. 4.7) that there is a close relation between the reversible cell voltage ΔE and the chemical drive $\mathcal{A}$ of the underlying total reaction. We will use our example to see how this works. We will rearrange Eq. (23.10):

$$-\mathcal{A} \cdot \Delta\xi = \left[\left(\mu(\mathrm{Cu}) - \mu(\mathrm{Cu^{2+}})\right) - \left(\mu(\mathrm{Zn}) - \mu(\mathrm{Zn^{2+}})\right)\right] \cdot \Delta\xi. \tag{23.12}$$

According to the defining equation for the redox potential, the following holds for both redox pairs:

$$\mu(\mathrm{Cu}) - \mu(\mathrm{Cu^{2+}}) = -2 \cdot \mathcal{F} \cdot E\left(\mathrm{Cu/Cu^{2+}}\right)$$

or

$$\mu(\mathrm{Zn}) - \mu(\mathrm{Zn^{2+}}) = -2 \cdot \mathcal{F} \cdot E\left(\mathrm{Zn/Zn^{2+}}\right).$$

By inserting into Eq. (23.12) and dividing both sides by $\Delta\xi$, we obtain

$$-\mathcal{A} = -2 \cdot \mathcal{F} \cdot E(\mathrm{Cu/Cu^{2+}}) + 2 \cdot \mathcal{F} \cdot E(\mathrm{Zn/Zn^{2+}}) = -2 \cdot \mathcal{F} \cdot \Delta E \tag{23.13}$$

and finally

$$\Delta E = -U = \frac{\mathcal{A}}{2\mathcal{F}}. \tag{23.14}$$

We can obtain the same result more simply if we equate the energy released during the reaction process with the energy emitted electrically $W_\xi = -\mathcal{A} \cdot \Delta\xi = U \cdot \nu_\mathrm{e} \mathcal{F} \Delta\xi$:

$$\Delta E = -U = \frac{\mathcal{A}}{\nu_\mathrm{e} \mathcal{F}}, \tag{23.15}$$

where ν_e is the number of electrons exchanged in a formula conversion.

Measurement of cell voltages for zero current flowing through the cell can therefore be used to determine the drive of a reaction. In practice, it is usually the standard values of these quantities that are determined and tabulated.

The reversible cell voltage is concentration dependent, just as the redox potential is. We will consider the general cell reaction

$$\mathrm{Rd} + \mathrm{Ox}^* \rightarrow \mathrm{Rd}^* + \mathrm{Ox}.$$

If we now apply Nernst's equation for redox potentials,

$$E(\mathrm{Ox}/\mathrm{Rd}) = \overset{\circ}{E}(\mathrm{Ox}/\mathrm{Rd}) + \frac{RT}{\nu_e \mathcal{F}} \cdot \ln \frac{c_r(\mathrm{Ox})}{c_r(\mathrm{Rd})}$$

or

$$E(\mathrm{Ox}^*/\mathrm{Rd}^*) = \overset{\circ}{E}(\mathrm{Ox}^*/\mathrm{Rd}^*) + \frac{RT}{\nu_e \mathcal{F}} \cdot \ln \frac{c_r(\mathrm{Ox}^*)}{c_r(\mathrm{Rd}^*)},$$

we obtain the following relation:

$$\begin{aligned} \Delta E &= E(\mathrm{Ox}^*/\mathrm{Rd}^*) - E(\mathrm{Ox}/\mathrm{Rd}) \\ &= \overset{\circ}{E}(\mathrm{Ox}^*/\mathrm{Rd}^*) + \frac{RT}{\nu_e \mathcal{F}} \cdot \ln \frac{c(\mathrm{Ox}^*)}{c(\mathrm{Rd}^*)} - \overset{\circ}{E}(\mathrm{Ox}/\mathrm{Rd}) - \frac{RT}{\nu_e \mathcal{F}} \cdot \ln \frac{c(\mathrm{Ox})}{c(\mathrm{Rd})} \end{aligned}$$

and then Nernst's equation for the total reaction

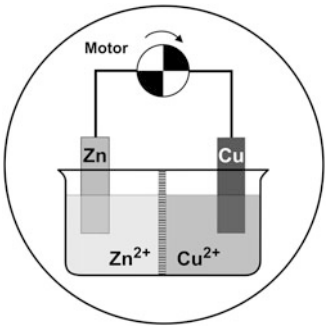
$$\Delta E = \Delta \overset{\circ}{E} + \frac{RT}{\nu_e \mathcal{F}} \cdot \ln \frac{c(\mathrm{Ox}^*) \cdot c(\mathrm{Rd})}{c(\mathrm{Rd}^*) \cdot c(\mathrm{Ox})} \tag{23.16}$$

with $\Delta \overset{\circ}{E} = \overset{\circ}{E}(\mathrm{Ox}^*/\mathrm{Rd}^*) - \overset{\circ}{E}(\mathrm{Ox}/\mathrm{Rd})$ as the basic value for the reversible cell voltage ΔE. The concentration dependency of ΔE in the case of a Daniell cell, for example, yields

$$\Delta E = \Delta \overset{\circ}{E} + \frac{RT}{2\mathcal{F}} \cdot \ln \frac{c_r(\mathrm{Cu}^{2+})}{c_r(\mathrm{Zn}^{2+})}.$$

If we replace the voltmeter in the experiment above (Fig. 23.5) with a load having a finite resistance R, possibly a small motor (Experiment 23.2), an electric current I will flow through the cell and the external circuit.

The Daniell cell discussed here is just one of many possible designs of galvanic cells (we will see more in Sect. 23.3). What they all have in common is that a chemical reaction (divided into two partial reactions) is used to drive an electron current. These cells make it possible to electrically utilize the energy released by



Experiment 23.2 *Daniell cell*: A small motor with a black and white disk (to show motion) can be driven using a Daniell cell.

chemical reactions. In the ideal case, there will be no disturbing side reactions occurring in the cell, so that chemical changes are only possible by the one reaction and only simultaneously with an exchange of electrons through the electrodes. In such cells, electron flow and chemical reaction are tightly coupled.

However, the electric voltage falls when the current flows through a load because the electrochemical equilibrium is disturbed. Electric and chemical potential differences are no longer in balance: More zinc ions at the zinc electrode go into the solution and copper ions discharge at the copper electrode.

Galvanic cells yield usable energy due to the spontaneous chemical reactions running inside them, but reversing the cell reaction must be forced by adding energy. This process, which is connected to chemical changes in the electrolyte, is called *electrolysis*.

23.3 Technically Important Galvanic Cells

In closing we will discuss some technically important galvanic cells. We will differentiate between primary cells, secondary cells, and fuel cells.

Primary Cells The processes running at the electrodes of primary cells (also called *primary batteries*) are irreversible, meaning that these batteries are not intended to be recharged. A well-known example of such a battery is the *zinc–manganese dioxide cell*, also known as the *zinc–carbon dry battery*, which is a further development of the galvanic cell patented by Georges Leclanché in 1866. It is made up of a zinc can acting as the anode and a cathode composed of a carbon rod surrounded by a mixture of manganese dioxide and carbon black (Fig. 23.7). The carbon black is added to increase the low electric conductivity of the manganese dioxide. The electrolyte is a paste of a 20 % solution of ammonium chloride thickened by starch or sawdust. This is why such galvanic elements are called dry batteries. The following simplified processes take place at the electrodes and in the electrolyte:

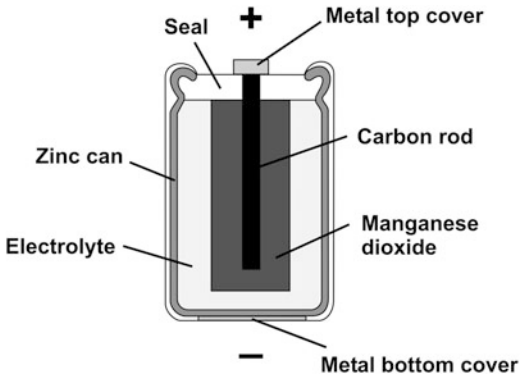


Fig. 23.7 Schematic cross section of a zinc–carbon dry battery.

$$\text{Anode}(-): \text{Zn|s} \rightarrow \text{Zn}^{2+}\text{|w} + 2\ \text{e}^-$$
$$\text{Cathode}(+): 2\ \text{MnO}_2\text{|s} + 2\ \text{H}_2\text{O|l} + 2\ \text{e}^- \rightarrow 2\ \text{MnOOH|s} + 2\ \text{OH}^-\text{|w}$$
$$\text{Electrolyte}: \text{Zn}^{2+}\text{|w} + 2\ \text{NH}_4^+\text{|w} + 2\ \text{Cl}^-\text{|w} + 2\ \text{OH}^-\text{|w} \rightarrow \text{Zn(NH}_3)_2\text{Cl}_2\text{|s} + 2\ \text{H}_2\text{O|l}$$
$$\text{Total reaction}: \text{Zn|s} + 2\ \text{MnO}_2\text{|s} + 2\ \text{NH}_4\text{Cl|w} \rightarrow 2\ \text{MnOOH|s} + \text{Zn(NH}_3)_2\text{Cl}_2\text{|s}$$

When a current flows, the manganese dioxide is reduced to MnOOH ($Mn^{4+} \rightarrow Mn^{3+}$), and the primarily formed zinc ions react with the electrolyte to form the hardly soluble complex $Zn(NH_3)_2Cl_2$.

At standard conditions, the redox potential of the zinc electrode equals −0.76 V. The redox potential of the manganese dioxide electrode is about +1.1 V and the nominal voltage at normal usage is around 1.5–1.6 V.

A fundamental improvement upon the zinc–carbon battery is the *alkaline-manganese dioxide battery* (short *alkaline battery*), which has a higher current-carrying capability and capacity and a longer shelf life. In this type of battery, potassium hydroxide solution is the electrolyte and the anode is zinc powder mixed with the electrolyte and a thickening agent to form a paste. This paste is put into a hollow cylinder made up of a compressed mixture of manganese dioxide and graphite. The cylinder lies against the inner wall of a steel can, forming the cathode. The electrode arrangement is opposite to that of the zinc–carbon battery.

The *zinc–mercury oxide button cell* (Fig. 23.8) uses a pellet of mercury oxide with a little graphite added to it for better conductivity as cathode. The anode of this battery is zinc powder (pressed or amalgamated). The electrolyte, a concentrated ZnO saturated potassium hydroxide solution, is on a cellulose felt. The following shows the simplified processes at the electrodes:

$$\text{Anode}(-): \text{Zn|s} + 2\ \text{OH}^-\text{|w} \rightarrow \text{Zn(OH)}_2\text{|s} + 2\ \text{e}^-$$
$$\text{Cathode}(+): \text{HgO} + \text{H}_2\text{O} + 2\ \text{e}^- \rightarrow \text{Hg} + 2\ \text{OH}^-$$
$$\text{Total reaction}: \text{Zn|s} + \text{HgO} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2\text{|s} + \text{Hg}$$

These button cells have a very long shelf life (up to 10 years) and their nominal voltage during discharge remains practically constant at 1.35 V. They have been normally used in small devices with low power demand such as watches, pocket

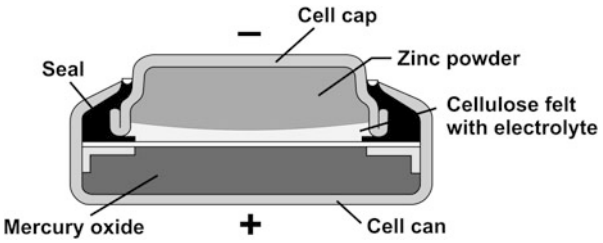


Fig. 23.8 Cross section of a zinc–mercury oxide button cell.

calculators, hearing aids, and cardiac pacemakers. However, due to the toxicity of the mercury, they are now replaced by the similar zinc–silver oxide cells or zinc–air cells.

Secondary Cells In contrast to what is the case in primary cells, it is mostly reversible processes that run at the electrodes of secondary cells (also called *secondary batteries* or *accumulators*). These cells are rechargeable.

The most common of this type of cell is the *lead-acid battery* that was developed in the nineteenth century. In its charged state, it is, in principle, made up of a lead anode and a lead oxide cathode. The electrolyte is sulfuric acid (25–30 %) saturated with lead sulfate. A simplified representation of the battery's charging and discharging processes shows the following reactions:

$$\text{Negative electrode: } \mathrm{Pb|s + SO_4^{2-}|w} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{PbSO_4|s + 2\,e^-}$$

$$\text{Positive electrode: } \mathrm{PbO_2|s + SO_4^{2-}|w + 4\ H_3O^+|w + 2\,e^-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{PbSO_4|s + 6\ H_2O|l}$$

$$\text{Total reaction: } \mathrm{Pb|s + PbO_2|s + 2\,H_2SO_4|w} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{2\,PbSO_4|s + 2\,H_2O|l}$$

When the battery is discharging, metallic lead oxidizes into lead sulfate and lead oxide is reduced to lead sulfate. Therefore, lead sulfate forms at both electrodes. At the same time, sulfuric acid is consumed and water is produced so that the density of sulfuric acid falls as discharging progresses. The state of the battery's charge can then be determined by this change of density.

Under standard conditions, the redox potential of the half-cell $\mathrm{Pb|PbSO_4|SO_4^{2-}}$ is -0.36 V, and that of the half-cell $\mathrm{PbO_2|PbSO_4|SO_4^{2-}}$ is +1.69 V. The nominal voltage of the cell is about 2 V. Depending upon the charge state and charging and discharging current, it can fluctuate between 1.75 and 2.4 V.

In order to recharge the battery, i.e., to "force" the reaction in the opposite direction, energy input is necessary. In the process, lead or lead oxide will reform at the lead sulfate electrodes.

When constructing a lead-acid battery it is important to remember that both electrode types need the largest surfaces possible so that the electrochemical reaction can occur at the highest possible rate. This can be attained, for example, by coating lead grids alloyed with antimony or calcium with a paste of Pb, PbO, and $\mathrm{PbSO_4}$. The plates then receive opposite charges in acid, forming lead sponge on

one side and porous lead oxide on the other (formation process). In order to avoid short circuiting through physical contact, the electrodes are separated by microporous plastic. Rechargeable lead-acid batteries can be produced in a closed construction (with valve), which is advantageous for transport and maintenance. In this case, the electrolyte is not liquid but fixed in a gel or a fibrous mat.

The most common use for rechargeable lead batteries in everyday life is for starting combustion engines in motor vehicles. Six cells in series deliver a terminal voltage of about 12 V. The constant running of the vehicle's generator keeps recharging the battery.

The negative electrodes in *nickel–cadmium batteries* are made up of finely distributed cadmium. The positive electrodes are composed of Ni(III) oxide hydroxide (with graphite or Ni powder added to enhance the conductivity). The electrolyte is usually a 20 % potassium hydroxide solution.

As the battery charges and discharges, the following simplified reactions take place at the electrodes:

$$\text{Negative electrode: } \mathrm{Cd|s + 2\,OH^-|w} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{Cd(OH)_2|s + 2\,e^-}$$

$$\text{Positive electrode: } \mathrm{2\,NiOOH|s + 2\,H_2O|l + 2\,e^-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{2\,Ni(OH)_2|s + 2\,OH^-|w}$$

In all, during discharging, metallic cadmium is transformed into the bivalent state (solid cadmium(II) hydroxide) by oxidation and trivalent nickel is reduced into bivalent nickel (solid nickel(II) hydroxide):

$$\text{Total reaction: } \mathrm{Cd|s + 2\,NiOOH|s + 2\,H_2O|l} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{Cd(OH)_2|s + 2\,Ni(OH)_2|s}$$

The nominal voltage of a nickel–cadmium battery is 1.2 V.

Gas-proof constructions are often designed like commercial batteries (including button cells), so they can replace the primary cells in portable electric and microelectric devices. Meanwhile, usage of nickel–cadmium batteries is strongly limited by law because of the dangers related to toxic cadmium.

A more environmentally friendly replacement for the Ni–Cd battery is the *nickel–metal-hydride battery* (NiMH), in which cadmium is replaced by a metal alloy that is able to store hydrogen reversibly. In the charged state, we have an anode made of metal hydride which is produced during the charging process by storing atomic hydrogen in a crystal lattice of the alloy (e.g., $\mathrm{La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}}$). As the cell discharges, the stored hydrogen oxidizes on the electrode's surface:

$$\text{Negative electrode: } \mathrm{MH|s + OH^-|w} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{M|s + H_2O|l + e^-}.$$

The cathode and electrolyte are identical to those in the NiCd battery. The total reaction is then:

$$\text{Total reaction: } \mathrm{MH|s + NiOOH|s} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{M|s + Ni(OH)_2|s}.$$

Again, the cell voltage is about 1.2 V, so the voltage of the NiMH cell is compatible with that of the NiCd cell. Along with its environmental advantages, it also has greater capacity and durability. However, its load capacity is lower.

Special accumulators for hybrid (electric) vehicles have been developed on the basis of nickel–metal hydride cells, i.e., cars powered by electric engines in combination with other energy converters (mostly combustion engines).

Fuel Cells In contrast to the galvanic cells we have discussed up to now, fuel cells have a constant feed of the substances consumed at the electrodes. This means that, theoretically, a current can be made to flow indefinitely. The term "fuel cell" actually means that substances can be converted there that are normally considered fuels and are otherwise burned for heating or for gaining energy. One well-known example of this is the so-called *hydrogen–oxygen fuel cell* (Fig. 23.9), which is used in manned space flight. This kind of cell uses hydrogen as the fuel and oxygen as the oxidizing agent. The electrolyte is a concentrated aqueous solution of KOH at elevated temperature and pressure [hence the alternative name alkaline fuel cell (AFC)]. The gases are conducted through porous plate electrodes (possibly made up of sinter nickel or pressed active carbon powder), the so-called gas diffusion

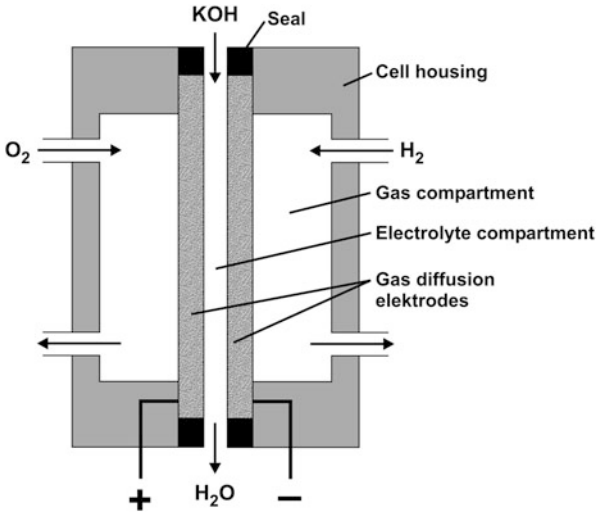


Fig. 23.9 Schematic of a hydrogen–oxygen fuel cell.

electrodes. In order to promote the splitting of hydrogen and oxygen molecules which precedes the actual reaction, the plates are coated with a small amount of a catalytic substance such as platinum or palladium.

The following simplified reactions then take place at the electrodes:

$$\begin{aligned}
&\text{Anode}(-): 2\,H_2|g + 4\,OH^-|w \rightarrow 4\,H_2O|l + 4\,e^- \\
&\text{Cathode}(+): O_2|g + 2\,H_2O|l + 4\,e^- \rightarrow 4\,OH^-|w \\
&\text{Total reaction}: 2\,H_2|g + O_2|g \rightarrow 2\,H_2O|l
\end{aligned}$$

The fuel oxidizes at the fuel cell's anode and oxygen reduces at the cathode. In total, the hydrogen undergoes a process of "cold combustion" where it turns into water. The cell voltage (at 200 °C and 4 MPa) is about 1.2 V.

Carbon monoxide as well as low-molecular organic compounds such as methane (CH_4) or methanol (CH_3OH) can also serve as fuels, and along with oxygen, air can also be an oxidizing agent. In place of KOH, solid electrolytes such as polymer membranes permeable only for protons [polymer electrolyte membrane fuel cells (PEMFC)] or oxygen-ion conducting oxide ceramics (yttria-stabilized zirconia) [solid oxide fuel cells (SOFC)] can also be used. One more possibility is melted salt as the electrolyte.

23.4 Cell Voltage Measurement and Its Application

We mentioned in Sect. 23.2 that galvanic cells can make the energy released by a chemical reaction usable, but they can also be utilized as a "measuring instrument" for the differences of redox potentials and therefore the electron potentials of various redox pairs. Moreover, because the electron potential itself is determined by the chemical potentials of the substances making up the redox pair, it is also possible to find the μ values as well as the drive $\mathcal{A}$ of the underlying total reaction with the help of galvanic cells. Reversible cell voltages measured with zero current can be used to determine these quantities and derived ones such as equilibrium constants.

Chemical potentials also depend upon the concentrations of substances, and in many cases, these dependencies are well known. Therefore, it is possible to utilize the measured voltages to find ion concentrations, especially solubilities and pH values (see Sect. 22.7). This method is called *potentiometry* and is widely applied in analytic chemistry.

Let us consider the simple example of determining the concentration of Ag^+ ions in an aqueous solution. We use a piece of silver as the electrode sensitive to Ag^+ ions, which we combine with the solution into a half-cell. Ag and the Ag^+ ions together form a redox pair to which we can assign the following electron potential:

$$\mu_e(\mathrm{Ag/Ag^+}) = \mu_{\mathrm{Ag}} - \mu_{\mathrm{Ag^+}} = \mu_{\mathrm{Ag}} - \overset{\circ}{\mu}_{\mathrm{Ag^+}} - RT\ln\frac{c_{\mathrm{Ag^+}}}{c^{\ominus}}.$$

Because, at a given temperature, μ_{Ag} and $\overset{\circ}{\mu}_{\mathrm{Ag^+}}$ have constant values, the electron potential and the corresponding Galvani potential difference developing between the metal and the solution depend only upon the concentration of Ag^+ ions in the solution (see also Sect. 22.5). If we now measure the Galvani potential difference relative to the standard hydrogen electrode to find the redox potential, we can apply Nernst's equation to determine the concentration $c_{\mathrm{Ag^+}}$ in the solution.

Measuring chemical potentials or determining concentrations using galvanic cells looks very promising at first. However, at many electrodes, potential differences develop only very gradually or can be disturbed by secondary reactions. These may consist of the formation of cover layers or may be the result of other redox pairs participating in the exchange of charge. Moreover, considerable deviations from the mass action equation—and therefore Nernst's equation—appear for ion concentrations above 10 mol m^{-3} (see also Sect. 6.2), so that the concentrations determined from measured cell voltage are often inexact. For this reason, potentiometry is combined with titration (*potentiometric titration*) because here the precision of the absolute value is unimportant. For example, the concentration of the ion that determines the potential may be changed by *precipitation titration*. We shall take a closer look at this by considering the determination of the silver content of a solution by titration with a KCl standard solution:

$$\mathrm{Ag^+|w + Cl^-|w \rightarrow AgCl|s.}$$

In this case, we are following the redox potential of the Ag/Ag^+ electrode ($E = E^{\ominus} + (RT^{\ominus}/\mathcal{F}) \cdot \ln c_{\mathrm{Ag^+}} = 0.7996 + 0.059 \cdot \lg c_{\mathrm{Ag^+}}$ V SHE at $T^{\ominus} = 298$ K) as a function of the addition of titrator (Fig. 23.10). When KCl standard solution is added drop by

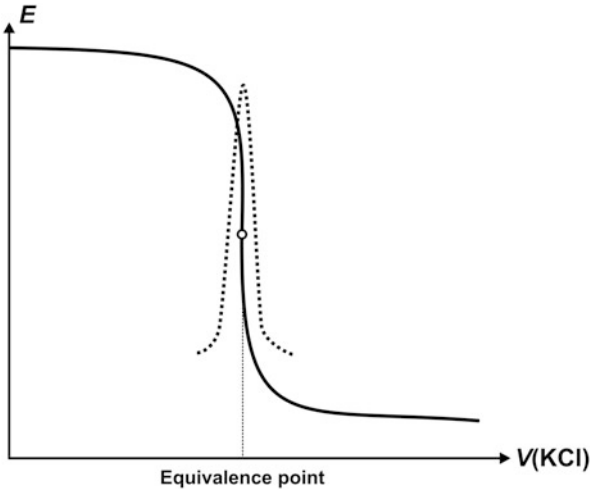


Fig. 23.10 Change of redox potential at an Ag/Ag^+ electrode during potentiometric titration of a silver-containing solution with a KCl standard solution (*solid line*) and first derivative of the titration curve (*dotted line*).

drop to the Ag^+ solution, the AgCl immediately precipitates and the concentration of Ag^+ ions in the recipient steadily decreases. This means that with each decrease of one decade of Ag^+ ion concentration, there is a lowering of potential of 59 mV. At the equivalence point, there is an abrupt fall of Ag^+ concentration and the corresponding potential, because at this point, one drop of KCl is enough to pretty much remove all the remaining Ag^+ ions. As a consequence, the concentration of Ag^+ ions is determined only by the solubility equilibrium of the silver chloride [$\overset{\circ}{\mathcal{K}}_{sd}(AgCl) = c_r(Ag^+) \cdot c_r(Cl^-) = 1.78 \times 10^{-10}$; compare also Sect. 6.6] and is therefore very low. According to the solubility product, a further addition of KCl solution continues to lower the Ag^+ concentration but, in parallel with the steady addition of KCl, the Ag^+ concentration drops now also steadily.

The equivalence point is determined by the inflection point of the titration curve. The first derivative of the titration curve is often used for a more exact determination of this point because a maximum is easier to localize than an inflection point. In practice, the quotient $\Delta E/\Delta V$ is plotted as a function of the given volume of titrator V. (ΔE corresponds to the difference of two consecutive measured values.)

The end point of *acid–base titrations*, *complexometric titrations*, or *redox titrations* can also be potentiometrically indexed by the use of suitable electrodes, for example, the glass electrode discussed in Sect. 22.7 in the case of acid–base reactions. The advantage of this method is that colored or cloudy solutions can also be titrated and it is simple to automate because an easily measured electric quantity participates.